



Supporting Information

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Supporting Information

Ketone Hydrosilylation with Sugar Silanes Followed by Intramolecular Aglycone Delivery: An Orthogonal Glycosylation Strategy

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All reagents were used as received unless otherwise noted. Solvents were purified under nitrogen using a solvent purification system (Innovative Technology, inc., Model # SPS-400-3 and PS-400-3). Ni(COD)₂ (Strem Chemicals, Inc., used as received), CuCl (Sigma-Aldrich, used as received), 1,3-dimesitylimidazolium chloride (IMes·HCl)¹ were stored and weighed in an inert atmosphere glovebox. Ti(O-*i*-Pr)₄ and Me₂Si(H)Cl were distilled and stored under inert atmosphere in Schlenk flasks. All nickel reactions were conducted in flame-dried glassware under a nitrogen atmosphere. ¹H and ¹³C spectra were obtained in CDCl₃ at rt, unless otherwise noted, on a Varian Mercury 400 or Varian Unity 500 MHz instrument. Chemical shifts of ¹H NMR spectra were recorded in parts per million (ppm) on the δ scale from an internal standard of residual chloroform (7.27 ppm). Chemical shifts of ¹³C NMR spectra were recorded in ppm from the central peak of CDCl₃ (77.0 ppm) on the δ scale. High resolution mass spectra (HRMS) were obtained on a VG-70-250-s spectrometer manufactured by Micromass Corp. (Manchester UK) at the University of Michigan Mass Spectrometry Laboratory.

General Procedure for the Preparation of Sugar Silanes

The respective 2-OH sugar (1.0 equiv) was dissolved in dry CH₂Cl₂ (0.2M) and cooled to 0 °C in an ice bath. Freshly distilled NEt₃ (2.0 equiv) was added and stirred for 3 minutes, Me₂Si(H)Cl (1.5 equiv) was then added. This was allowed to stir for 4 hours then volatiles were removed by rotary evaporation, the resulting oil was extracted from NaHCO₃ (aq.) (diluted over ice) 3 times with CH₂Cl₂. The combined organic extracts were dried quickly over MgSO₄, filtered, concentrated, and the resulting oil was either used directly or stored frozen in C₆H₆. Note – the sugar silanes are stable for months when stored frozen in benzene, alternatively the corresponding 2-OH sugars are very stable to be stored for long periods of time on the bench top.

General Procedure for the Ni(COD)₂/IMes Promoted Hydrosilylation of Ketones

A solid mixture of Ni(COD)₂ (10%), IMes·HCl (10%), and KO-*t*-Bu (10%) was dissolved in dry THF (0.02M) at rt under an inert atmosphere (N₂), and stirred for 10-15 minutes until the catalyst mixture was a dark blue color. Ti(O*i*-Pr)₄ (1.1-2.2 equiv) was

then added to the catalyst mixture followed by the addition of the sugar silane (1.1 equiv), and ketone (1.0 equiv) as a solution in dry THF (0.2M). Upon completion of the reaction, as monitored by TLC, the reaction mixture was filtered through a short plug of silica gel with a mixture of EtOAc/hexanes and concentrated by rotary evaporation. The resulting residue was purified via flash chromatography (SiO₂) to afford the desired product. Note – When doing the site-selective hydrosilylation of a ketone in the presence of a free hydroxyl group, the use of 2.2 equiv of Ti(O-*i*-Pr)₄ and a 0.05 M solution in THF results in higher yields of the desired product.

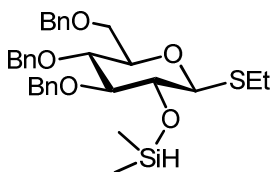
General Procedure for the CuCl/IMes Promoted Hydrosilylation of Ketones

A solid mixture of CuCl (5%), IMes·HCl (5%) and KO-*t*-Bu (10%) was dissolved in dry toluene (0.015M) at rt under an inert atmosphere (N₂), and stirred for 20 minutes. A mixture of ketone (1.0 equiv) and silane (1.1 equiv) was dissolved in dry toluene (0.2M), the catalyst was then added to this mixture as a solution in a minimum of dry toluene. Upon completion of the reaction, as monitored by TLC, the reaction mixture was filtered through a short plug of silica gel with a mixture of EtOAc/Hexanes and concentrated by rotary evaporation. The resulting residue was purified via flash chromatography (SiO₂) to afford the desired product.

General Procedure for the NIS/TMSOTf Mediated Glycosylation of Silyl-linked Compounds

The respective silyl-linked compound (1.0 equiv) was dissolved in dry CH₂Cl₂ (0.02M) and cooled to -40 °C. *N*-iodosuccinimide (NIS) (1.3-1.4 equiv) and 2,6-di-*tert*-butyl-4-methyl pyridine (2,6-DTBMP) (2.0-4.0 equiv) were added and stirred for 3 minutes. To this solution, trimethylsilyl trifluoromethanesulfonate (TMSOTf) (1.2-2.4 equiv) was added, this is stirred for 10-15 minutes and then warmed to 0 °C. Upon disappearance of the silyl-linked compound, as monitored by TLC (generally 30 to 90 min), *n*-Bu₄NF (5-10 equiv, 1M THF) was added, and the reaction was warmed to rt and stirred overnight. The reaction mixture was then quenched with sat. Na₂S₂O₃ (aq.) and extracted three times from sat. NH₄Cl (aq.) with EtOAc. The combined organic extracts were dried over MgSO₄, filtered, concentrated, and purified by flash chromatography on SiO₂ to afford the desired product.

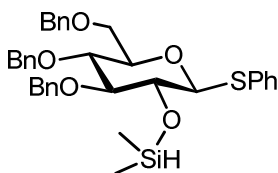
Ethyl 2-*O*-dimethylsilane-3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (Scheme 1, compound 1a)



Following the general procedure, ethyl 3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (1.237 g, 2.50 mmol),² NEt₃ (0.697 mL, 5.00 mmol), and Me₂Si(H)Cl (0.416 mL, 3.75

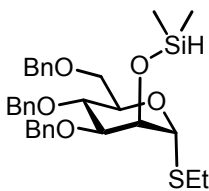
mmol) were stirred for 4 hours at 0 °C. The product (1.38 g, 2.50 mmol, 100%) was obtained as a red oil after aqueous work up. ¹H NMR (500MHz, CDCl₃) δ 7.25-7.28 (m, 13H), 7.12-7.16 (m, 2H), 4.91 (d, *J* = 11.5 Hz, 1H), 4.85 (d, *J* = 11.0 Hz, 1H), 4.82 (sept, *J* = 3.0 Hz, 1H), 4.78 (d, *J* = 10.5 Hz, 1H), 4.61 (d, *J* = 12.5 Hz, 1H), 4.553 (d, *J* = 12.5 Hz, 1H), 4.546 (d, *J* = 11.0 Hz, 1H), 4.37 (d, *J* = 9.0 Hz, 1H anomeric), 3.75 (dd, *J* = 10.5, 1.5 Hz, 1H), 3.69 (dd, *J* = 11.0, 4.5 Hz, 1H), 3.53-3.62 (m, 3H), 3.49 (ddd, *J* = 9.5, 5.0, 2.0 Hz, 1H), 2.77 (dq, *J* = 12.5, 7.5 Hz, 1H), 2.71 (dq, *J* = 12.0, 8.0 Hz, 1H), 1.32 (t, *J* = 7.5 Hz, 3H), 0.31 (d, *J* = 3.0 Hz, 3H), 0.25 (d, *J* = 2.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 138.5, 138.2, 138.0, 128.34, 128.30, 128.27, 127.9, 127.71, 127.69, 127.52, 127.48, 127.45, 87.2, 86.1, 79.2, 77.9, 75.9, 75.6, 75.0, 73.4, 69.1, 24.7, 15.0, -0.6, -0.8; IR (film, cm⁻¹) 2956, 2926, 2864, 2129, 1651, 1385, 1083; HRMS (ES) *m/z* calcd for C₃₁H₄₀O₅SSi [M+Na]⁺ 575.2263, found 575.2269.

Phenyl 2-*O*-dimethylsilane-3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (Scheme 1, compound 1b)



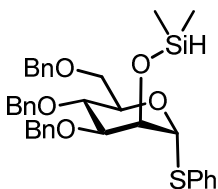
Following the general procedure, phenyl 3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (1.00 g, 1.8 mmol),² NEt₃ (0.513 μL, 3.7 mmol), and Me₂Si(H)Cl (307 μL, 2.8 mmol) were stirred for 4 hours at 0 °C. The product (1.10 g, 1.8 mmol, 99%) was obtained as a red oil after aqueous work up. ¹H NMR (500 MHz, CDCl₃) δ 7.56-7.59 (m, 2H), 7.24-7.38 (m, 16H), 7.15-7.20 (m, 2H), 4.91 (d, *J* = 11.0 Hz, 1H), 4.87 (d, *J* = 11.5 Hz, 1H), 4.85 (sept, *J* = 3.0 Hz, 1H), 4.79 (d, *J* = 10.5 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.61 (d, *J* = 9.5 Hz, 1H anomeric) 4.59 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 12.5 Hz, 1H), 3.80 (dd, *J* = 10.5, 1.5 Hz, 1H), 3.73 (dd, *J* = 11.0, 5.0 Hz, 1H), 3.67 (t, *J* = 9.0 Hz, 1H), 3.65 (t, *J* = 9.0 Hz, 1H), 3.58 (t, *J* = 8.25 Hz, 1H), 3.54 (ddd, *J* = 9.5, 4.5, 1.5 Hz, 1H), 0.29 (d, *J* = 2.5 Hz, 3H), 0.24 (d, *J* = 3.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 138.4, 138.2, 138.0, 134.1, 131.5, 128.8, 128.4, 128.3, 127.9, 127.8, 127.7, 127.53, 127.49, 127.48, 127.2, 88.8, 87.2, 79.2, 77.8, 75.6, 75.1, 75.0, 73.4, 69.0, -0.6, -0.9; IR (film, cm⁻¹) 3060, 3028, 2864, 2129, 1452, 1362, 1066; HRMS (ES) *m/z* calcd for C₃₅H₄₀O₅SSi [M+Na]⁺ 623.2263, found 623.2274.

Ethyl 2-*O*-dimethylsilane-3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (Scheme 1, compound 2a)



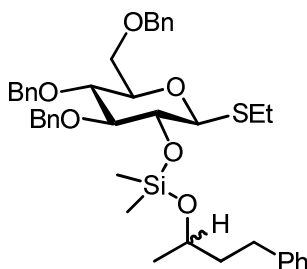
Following the general procedure, ethyl 3,4,6-tri-*O*-benzyl-1-thio- α -D-mannopyranoside (1.74 g, 3.5 mmol),² NEt₃ (0.98 mL, 7.0 mmol), and Me₂Si(H)Cl (587 μ L, 5.3 mmol) were stirred for 4 hours at 0 °C. The product (1.93 g, 3.5 mmol, 100%) was obtained as a red oil after aqueous work up. ¹H NMR (500MHz, CDCl₃) δ 7.25-7.39 (m, 13H), 7.15-7.18 (m, 2H), 5.27 (d, *J* = 2.0 Hz, 1H anomeric), 4.84 (d, *J* = 11.0 Hz, 1H), 4.76 (sept, *J* = 2.5 Hz, 1H), 4.73 (d, *J* = 11.5 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 11.5 Hz, 1H), 4.50 (d, *J* = 11.5 Hz, 1H), 4.49 (d, *J* = 11.0 Hz, 1H), 4.18 (t, *J* = 2.25 Hz, 1H), 4.13 (ddd, *J* = 10.0, 5.0, 2.0 Hz, 1H), 3.95 (t, *J* = 9.5 Hz, 1H), 3.76-3.83 (m, 2H), 3.70 (dd, *J* = 11.0, 2.0 Hz, 1H), 2.67 (dq, *J* = 13.0, 7.0 Hz, 1H), 2.59 (dq, *J* = 13.0, 7.5 Hz, 1H), 1.29 (t, *J* = 7.5 Hz, 3H), 0.26 (d, *J* = 2.5 Hz, 3H), 0.24 (d, *J* = 2.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 138.43, 138.40, 138.1, 128.28, 128.25, 128.20, 127.89, 127.65, 127.59, 127.50, 127.4, 85.0, 80.7, 74.9, 74.6, 73.2, 72.5, 72.2, 72.1, 69.1, 25.2, 15.0, -0.6, -0.7; IR (film, cm⁻¹) 3030, 2870, 2122, 1453, 1384, 1250, 1097; HRMS (ES) *m/z* calcd for C₃₁H₄₀O₅SSi [M+Na]⁺ 575.2263, found 575.2273.

Phenyl 2-*O*-dimethylsilane-3,4,6-tri-*O*-benzyl-1-thio- α -D-mannopyranoside (Scheme 1, compound 2b)



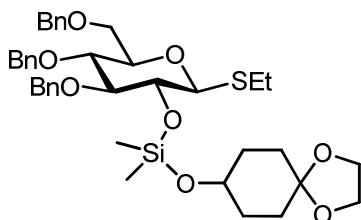
Following the general procedure, phenyl 3,4,6-tri-*O*-benzyl-1-thio- α -D-mannopyranoside (0.765 g, 1.4 mmol),² NEt₃ (0.390 mL, 2.8 mmol), and Me₂Si(H)Cl (0.233 mL, 2.1 mmol) were stirred for 4 hours at 0 °C. The product (0.828 g, 1.4 mmol, 98%), was obtained as a red oil after aqueous work up. ¹H NMR (500 MHz, CDCl₃) δ 7.48-7.51 (m, 2H), 7.39-7.42 (m, 2H), 7.23-7.37 (m, 14H), 7.18-7.21 (m, 2H), 5.50 (d, *J* = 1.5 Hz, 1H anomeric), 4.87 (d, *J* = 11.0 Hz, 1H), 4.78 (d, *J* = 11.5 Hz, 1H), 4.76 (sept, *J* = 3.0 Hz, 1H), 4.68 (d, *J* = 11.5 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 11.0 Hz, 1H), 4.48 (d, *J* = 12.0 Hz, 1H), 4.34 (t, *J* = 2.0 Hz, 1H), 4.29 (ddd, *J* = 9.5, 4.5, 1.5 Hz, 1H), 4.00 (t, *J* = 9.5 Hz, 1H), 3.79-3.86 (m, 2H), 3.74 (dd, *J* = 11.0, 2.0 Hz, 1H), 0.26 (d, *J* = 3.0 Hz, 3H), 0.22 (d, *J* = 3.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 138.36, 138.31, 134.4, 131.3, 128.9, 128.32, 128.28, 128.18, 127.9, 127.65, 127.57, 127.4, 127.2, 88.7, 80.5, 75.0, 74.5, 73.2, 72.8, 72.5, 72.3, 69.1, -0.6, -0.7; IR (film, cm⁻¹) 3061, 3030, 2869, 2123, 1453, 1368, 1251, 1101; HRMS (ES) *m/z* calcd for C₃₅H₄₀O₅SSi [M+Na]⁺ 623.2263, found 623.2248.

Ethyl 2-*O*-dimethyl[(4-phenylbutan-2-yloxy)silane]-3,4,6-tri-*O*-benzyl-1-thio- β -D-glucopyranoside (Table 1, compound 4a)



Following the general procedure, **1a** (182 mg, 0.33 mmol), freshly distilled (bulb-to-bulb) benzylacetone (45 μ L, 0.30 mmol), Ni(COD)₂ (8 mg, 0.03 mmol), IMes·HCl (10 mg, 0.03 mmol), and KO-*t*-Bu (3 mg, 0.03 mmol) were stirred at rt for 13 hours. The desired product was obtained as an inseparable mixture of diastereomers (54:46) (204 mg, 0.29 mmol, 97%, 54:46) as a clear oil, upon purification by flash chromatography on SiO₂ (10% EtOAc/Hex). ¹H NMR (500 MHz, CDCl₃) δ 7.24-7.40 (m, 16H), 7.14-7.19 (m, 2H), 7.09-7.13 (m, 2H), 4.98 (d, *J* = 11.5 Hz, 1H), 4.89 (d, *J* = 11.5 Hz, 0.5H), 4.88 (d, *J* = 11.0 Hz, 0.5H), 4.75 (d, *J* = 10.5 Hz, 0.5H), 4.74 (d, *J* = 11.0 Hz, 0.5H), 4.52-4.63 (m, 3H), 4.40 (d, *J* = 9.5 Hz, 0.5H anomeric), 4.39 (d, *J* = 9.5 Hz, 0.5H anomeric), 4.00-4.08 (m, 1H), 3.67-3.78 (m, 3H), 3.54-3.64 (m, 2H), 3.48-3.52 (m, 1H), 2.66-2.80 (m, 3H), 2.55-2.62 (m, 1H), 1.74-1.84 (m, 1H), 1.65-1.73 (m, 1H), 1.31 (t, *J* = 7.5 Hz, 3H), 1.21 (d, *J* = 6.0 Hz, 1.5H), 1.19 (d, *J* = 6.0 Hz, 1.5H), 0.23 (s, 1.5H), 0.22 (s, 1.5H), 0.19 (s, 1.5H), 0.18 (s, 1.5H), Note – diastereomers are reported as a 1:1 ratio of the total amount of protons; ¹³C NMR (100 MHz, CDCl₃) major and minor diastereomer signals reported δ 142.53, 142.50, 138.8, 138.2, 137.9, 128.3, 128.32, 128.24, 128.19, 127.9, 127.7, 127.5, 127.26, 127.24, 127.21, 127.1, 125.58, 125.56, 87.1, 86.2, 79.1, 78.2, 75.18, 75.15, 74.9, 74.48, 74.43, 73.4, 69.1, 68.3, 68.1, 41.0, 32.04, 32.02, 24.7, 23.7, 23.6, 15.1, -0.8, -0.9, -1.2, -1.3; IR (film, cm⁻¹) 3029, 2965, 2923, 2865, 1496, 1453, 1366, 1256, 1134, 1086; HRMS (ES) *m/z* calcd for C₄₁H₅₂O₆SSi [M+Na]⁺ 723.3152, found 723.3162.

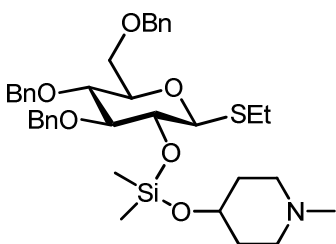
Ethyl 2-*O*-[(1,4-dioxaspiro[4.5]decan-8-yloxy)dimethylsilane]-3,4,6-tri-*O*-benzyl-1-thio- β -D-glucopyranoside (Table 1, compound **4b)**



Following the general procedure, **1a** (182 mg, 0.33 mmol), 1,4-cyclohexanedione monoethylene acetal (47 mg, 0.30 mmol), Ni(COD)₂ (8 mg, 0.03 mmol), IMes·HCl (10 mg, 0.03 mmol), KO-*t*-Bu (3.4 mg, 0.03 mmol), and Ti(O-*i*-Pr)₄ (98 μ L, 0.33 mmol) were stirred for 3 hr at rt. The product (197 mg, 0.28 mmol, 93%) was obtained as a viscous yellow oil after purification by flash chromatography on SiO₂ (10 to 20% EtOAc/Hex). ¹H NMR (500 MHz, CDCl₃) δ 7.24-7.38 (m, 13H), 7.08-7.12 (m, 2H), 4.93 (d, *J* = 11.5 Hz, 1H), 4.89 (d, *J* = 11.5 Hz, 1H), 4.73 (d, *J* = 11.0 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 11.0 Hz, 1H), 4.40 (d, *J* = 9.5 Hz, 1H)

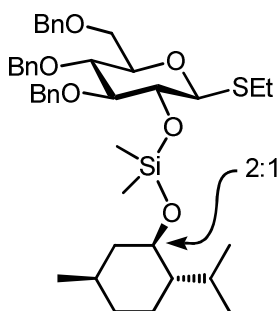
anomeric), 4.01 (tt, $J = 7.5, 3.5$ Hz, 1H), 3.90-3.96 (m, 4H), 3.75 (dd, $J = 11.0, 2.0$ Hz, 1H), 3.66-3.73 (m, 2H), 3.60 (t, $J = 9.25$, 1H), 3.55 (t, $J = 8.75$ Hz, 1H), 3.49 (ddd, $J = 9.5, 5.0, 2.0$ Hz, 1H), 2.77 (dq, $J = 12.75, 7.5$ Hz, 1H), 2.71 (dq, $J = 13.5, 7.5$ Hz, 1H), 1.64-1.85 (m, 6H), 1.46-1.54 (m, 2H), 1.31 (t, $J = 7.5$ Hz, 3H), 0.21 (s, 3H), 0.16 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.7, 138.2, 138.0, 128.32, 128.30, 128.2, 127.9, 127.72, 127.69, 127.5, 127.2, 127.0, 108.4, 87.0, 86.2, 79.1, 78.3, 75.1, 74.9, 74.4, 73.4, 69.1, 68.3, 64.17, 64.15, 32.03, 32.00, 31.34, 31.32, 24.6, 15.0, -0.9, -1.3; IR (film, cm^{-1}) 3030, 2929, 1497, 1453, 1363, 1255, 1094; HRMS (ES) m/z calcd for $\text{C}_{39}\text{H}_{52}\text{O}_8\text{SSi}$ $[\text{M}+\text{Na}]^+$ 731.3050, found 731.3062.

Ethyl 2-*O*-[4-(dimethylsilyloxy)-1-methylpiperidine]-3,4,6-tri-*O*-benzyl-1-thio- β -D-glucopyranoside (Table 1, compound 3c)



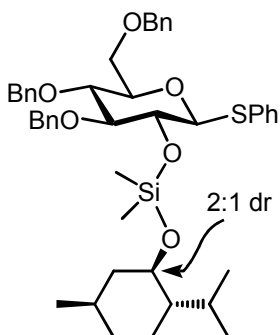
Following the general procedure, **1a** (182 mg, 0.33 mmol), N-methyl-4-piperidone (37 μL , 0.30 mmol), $\text{Ti}(\text{O}-i\text{-Pr})_4$ (98 μL , 0.33 mmol), $\text{Ni}(\text{COD})_2$ (8 mg, 0.03 mmol), $\text{IMes}\cdot\text{HCl}$ (10 mg, 0.03 mmol), and $\text{KO}-t\text{-Bu}$ (3 mg, 0.03 mmol) were stirred for 6 hours at rt. The product (200 mg, 0.30 mmol, 100%) was obtained after flash chromatography on SiO_2 (15% MeOH/EtOAc w/ $\sim 1\%$ NEt_3) as a viscous light orange oil. ^1H NMR (500 MHz, CDCl_3) δ 7.24-7.38 (m, 13H), 7.08-7.12 (m, 2H), 4.95 (d, $J = 11.0$ Hz, 1H), 4.89 (d, $J = 11.5$ Hz, 1H), 4.73 (d, $J = 10.5$ Hz, 1H), 4.61 (d, $J = 12.0$ Hz, 1H), 4.56 (d, $J = 12.0$ Hz, 1H), 4.53 (d, $J = 10.5$ Hz, 1H), 4.39 (d, $J = 9.5$ Hz, 1H anomeric), 3.88 (br s, 1H), 3.75 (dd, $J = 11.0, 1.5$ Hz, 1H), 3.67-3.72 (m, 2H), 3.60 (t, $J = 9.25$ Hz, 1H), 3.55 (t, $J = 8.75$ Hz, 1H), 3.49 (ddd, $J = 10.0, 5.0, 1.5$ Hz, 1H), 2.77 (dq, $J = 12.5, 7.5$ Hz, 1H), 2.72 (dq, $J = 12.5, 7.5$ Hz, 1H), 2.65 (br s, 2H), 2.23 (s, 3H), 1.98-2.10 (m, 2H), 1.74-1.86 (m, 2H), 1.58 (m, 2H), 1.32 (t, $J = 7.25$ Hz, 3H), 0.22 (s, 3H), 0.17 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.7, 138.1, 137.9, 128.33, 128.31, 128.2, 127.9, 127.7, 127.5, 127.3, 127.1, 87.0, 86.1, 79.1, 78.2, 75.1, 74.9, 74.5, 73.4, 69.1, 52.9, 45.9, 34.2, 24.6, 15.1, -0.9, -1.3; IR (film, cm^{-1}) 3030, 2927, 2864, 2780, 1452, 1362, 1255, 1148, 1087; HRMS (ES) m/z calcd for $\text{C}_{37}\text{H}_{51}\text{NO}_6\text{SSi}$ $[\text{M}+\text{H}]^+$ 666.3285, found 666.3284.

Ethyl 2-*O*-[[(1R,2S,5R)-2-isopropyl-5-methylcyclohexyloxy]dimethylsilane]-3,4,6-tri-*O*-benzyl-1-thio- β -D-glucopyranoside (Table 1, compound 4d)



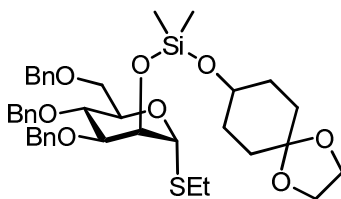
Following the general procedure, **1a** (243 mg, 0.30 mmol), (-)-menthone³ (62 mg, 0.40 mmol), CuCl (2 mg, 0.015 mmol), IMes·HCl (7 mg, 0.015 mmol) and NaO-*t*-Bu (3 mg, 0.03 mmol) were stirred for 8 hours at rt to give the product as an inseparable 2:1 mixture of diastereomers. The product (192 mg, 0.27 mmol, 68%, 2:1) was obtained as a clear oil upon purification by flash chromatography on SiO₂ (10% EtOAc/Hex). ¹H NMR (500 MHz, CDCl₃) δ 7.23-7.41 (m, 13 H), 7.07-7.14 (m, 2H), 5.01 (d, *J* = 11.0 Hz, 0.67H), 4.97 (d, *J* = 11.5 Hz, 0.33H), 4.88 (d, *J* = 12.0 Hz, 0.33H), 4.86 (d, *J* = 11.0 Hz, 0.67H), 4.75 (d, *J* = 11.0 Hz, 0.67H), 4.72 (d, *J* = 11.0 Hz, 0.33H), 4.50-4.63 (m, 3 H), 4.39 (d, *J* = 9.5 Hz, 0.67H anomeric), 4.38 (d, *J* = 9.5 Hz, 0.33H anomeric), 4.26 (br s, 0.33H), 3.66-3.78 (m, 3H), 3.53-3.62 (m, 2.67H), 3.48-3.53 (m, 1H), 2.68-2.81 (m, 2H), 2.20 (septd, *J* = 7.0, 2.5 Hz, 0.67H), 1.99-2.04 (m, 0.67H), 1.78-1.88 (m, 0.67H), 1.48-1.65 (m, 2.33H), 1.26-1.40 (m, 1H), 1.32 (t, *J* = 7.5 Hz, 3H_{major}), 1.31 (t, *J* = 7.5 Hz, 3H_{minor}), 0.74-1.15 (m, 10.67H), 0.73 (d, *J* = 7.0 Hz, 3H_{major}), 0.23 (s, 3H_{major}), 0.19 (s, 3H_{minor}), 0.15 (s, 3H_{major + minor}), Note – diastereomers are reported as a 2:1 ratio of the total amount of protons, the stereochemistry of the major diastereomer and the dr of the reduction was determined on a crude reaction mixture of the silyl-linked compound after complete desilylation by *n*-Bu₄NF and comparison to known compounds;^{4,5} ¹³C NMR (100 MHz, CDCl₃) major and minor diastereomer signals reported δ 138.9, 138.8, 138.24, 138.22, 138.0, 128.34, 128.31, 128.16, 128.13, 127.94, 127.89, 127.7, 127.5, 127.3, 127.2, 127.11, 127.96, 87.2, 87.0, 86.4, 86.3, 79.1, 78.3, 78.2, 75.2, 75.1, 74.9, 74.5, 74.3, 73.4, 72.6, 69.3, 69.2, 68.8, 49.7, 48.8, 45.4, 43.1, 42.6, 35.3, 34.5, 31.6, 28.7, 25.5, 25.2, 24.8, 24.6, 24.0, 22.8, 22.4, 22.2, 21.2, 21.1, 20.9, 15.9, 15.0, -0.4, -1.0, -1.5; IR (film, cm⁻¹) 3029, 2953, 2921, 2866, 1453, 1365, 1254, 1067; HRMS (ES) *m/z* calcd for C₄₁H₅₈O₆SSi [M+Na]⁺ 729.3621, found 729.3639.

Phenyl 2-*O*-[((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyloxy)dimethylsilane]-3,4,6-tri-*O*-benzyl-1-thio-β-*D*-glucopyranoside (Table 1, compound 4e)



Following the general procedure, **1b** (198 mg, 0.33 mmol), (-)-menthone³ (46 mg, 0.30 mmol), CuCl (2 mg, 0.015 mmol), IMes·HCl (5 mg, 0.015 mmol), and NaO-*t*-Bu (3 mg, 0.03 mmol) were stirred for 5 hours at rt to give the desired product as an inseparable 2:1 mixture of diastereomers. The product (144 mg, 0.19 mmol, 64%, 2:1) was obtained as a clear viscous oil upon purification by flash chromatography on SiO₂ (5% EtOAc/Hex). ¹H NMR (500 MHz, CDCl₃) δ 7.52-7.57 (m, 2H), 7.21-7.41 (m, 16H), 7.10-7.17 (m, 2H), 5.02 (d, *J* = 11.0 Hz, 0.67H), 4.98 (d, *J* = 11.5 Hz, 0.33H), 4.89 (d, *J* = 11.5 Hz, 0.33H), 4.86 (d, *J* = 10.5 Hz, 0.67H), 4.78 (d, *J* = 11.0 Hz, 0.67H), 4.73 (d, *J* = 10.5 Hz, 0.33H), 4.52-4.66 (m, 4H), 4.27 (br s, 0.33H), 3.76-3.86 (m, 2H), 3.69-3.74 (m, 1H), 3.51-3.66 (m, 3.67H), 2.21 (septd, *J* = 6.75, 2.25 Hz, 0.67H), 2.01 (d, *J* = 12.0 Hz, 0.67H), 1.80-1.89 (m, 0.67H), 1.48-1.64 (m, 2.33H), 1.26-1.41 (m, 1.33H), 1.09-1.18 (m, 0.67H), 0.75-1.07 (m, 5.67H), 0.87 (d, *J* = 7.0 Hz, 3H_{minor}), 0.85 (d, *J* = 7.0 Hz, 3H_{major}), 0.84 (d, *J* = 6.5 Hz, 3H_{minor}), 0.74 (d, *J* = 7.0 Hz, 3H_{major}), 0.25 (s, 3H_{major}), 0.20 (s, 3H_{minor}), 0.16 (s, 3H_{minor}), 0.13 (s, 3H_{major}). Note – diastereomers are reported as a 2:1 ratio of the total amount of protons, the stereochemistry of the major diastereomer and the dr of the reduction was determined on a crude reaction mixture of the silyl-linked compound after complete desilylation by *n*-Bu₄NF and comparison to known compounds;^{4,5} ¹³C NMR (100 MHz, CDCl₃) δ major and minor diastereomer signals reported 138.8, 138.7, 138.26, 138.24, 138.0, 137.0, 134.5, 131.1, 131.0, 128.8, 128.37, 128.33, 128.30, 128.18, 128.15, 127.90, 127.8, 127.73, 127.69, 127.67, 127.52, 127.51, 127.3, 127.2, 126.97, 126.96, 126.91, 89.1, 88.8, 87.2, 87.0, 79.03, 78.98, 78.16, 78.12, 75.2, 75.1, 74.9, 73.9, 73.8, 73.4, 72.7, 69.14, 69.07, 68.9, 49.7, 48.8, 45.4, 43.2, 35.2, 34.5, 31.6, 28.7, 25.6, 25.2, 24.0, 22.8, 22.3, 22.2, 21.2, 21.1, 20.9, 15.9, -0.4, -1.1, -1.2, -1.4; IR (film, cm⁻¹) 3030, 2953, 2919, 2867, 1454, 1383, 1256, 1067; HRMS (ES) *m/z* calcd for C₄₅H₅₈O₆SSi [M+Na]⁺ 777.3621, found 777.3635.

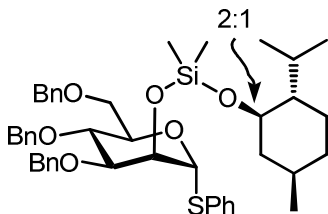
Ethyl 2-*O*-[(1,4-dioxaspiro[4.5]decan-8-yloxy)dimethylsilane]-3,4,6-tri-*O*-benzyl-1-thio- α -D-mannopyranoside (Table 1, compound **5a)**



Following the general procedure, **2a** (182 mg, 0.33 mmol), 1,4-cyclohexanedione monoethylene acetal (47 mg, 0.30 mmol), Ti(O-*i*-Pr)₄ (98 μ L, 0.33 mmol), Ni(COD)₂ (8 mg, 0.03 mmol), IMes·HCl (10 mg, 0.03 mmol), and KO-*t*-Bu (3 mg, 0.03 mmol) were stirred at room temperature for 4 hours. The product (183 mg, 0.26 mmol, 86%) was obtained as a colorless oil after purification by flash chromatography on SiO₂ (10 to 20% EtOAc/Hex). ¹H NMR (500 MHz, CDCl₃) δ 7.24-7.37 (m, 13H), 7.15-7.18 (m, 2H), 5.28 (d, *J* = 1.5 Hz, 1H anomeric), 4.83 (d, *J* = 10.5 Hz, 1H), 4.71 (d, *J* = 11.5 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.64 (d, *J* = 11.5 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.50 (d, *J* = 10.5 Hz, 1H), 4.28 (t, *J* = 2.25 Hz, 1H), 4.13 (ddd, *J* = 10.0, 5.0, 1.5 Hz, 1H), 3.90-4.00 (m, 5H), 3.82 (dd, *J* = 11.0, 5.0 Hz, 1H), 3.77 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.71 (dd, *J* =

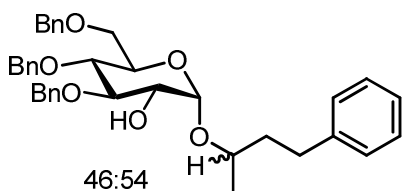
10.5, 1.5 Hz, 1H), 2.66 (dq, $J = 13.0, 7.5$ Hz, 1H), 2.58 (dq, $J = 13.0, 7.5$ Hz, 1H), 1.64-1.86 (m, 6H), 1.46-1.55 (m, 2H), 0.17 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.49, 138.47, 138.3, 128.27, 128.25, 128.21, 127.9, 127.8, 127.6, 127.52, 127.49, 127.36, 108.4, 85.4, 80.3, 74.9, 74.8, 73.2, 72.2, 71.0, 69.2, 68.1, 64.20, 64.17, 32.05, 32.00, 31.2, 25.2, 15.0, -1.5, -1.7; IR (film, cm^{-1}) 3030, 2938, 2874, 1452, 1378, 1256, 1099, 1036; HRMS (ES) m/z calcd for $\text{C}_{39}\text{H}_{52}\text{O}_8\text{SSi}$ $[\text{M}+\text{Na}]^+$ 731.3050, found 731.3055.

Phenyl 2-*O*-[((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyloxy)dimethylsilane]-3,4,6-tri-*O*-benzyl-1-thio- α -D-mannopyranoside (Table 1, compound 5b)



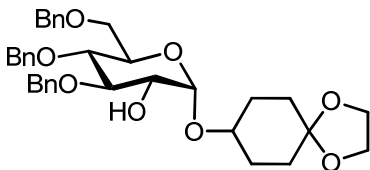
Following the general procedure, **2b** (198 mg, 0.33 mmol), (-)-menthone³ (46 mg, 0.30 mmol), CuCl (1.5 mg, 0.015 mmol), IMes·HCl (5 mg, 0.015 mmol), and NaO-*t*-Bu (3 mg, 0.03 mmol) were stirred for 4 hours at rt to give the desired product as an inseparable 2:1 mixture of diastereomers. The product (171 mg, 0.23 mmol, 75%, 2:1) was isolated as a colorless oil upon purification by flash chromatography on SiO_2 (5% EtOAc/Hex). ^1H NMR (500 MHz, CDCl_3) δ 7.47-7.51 (m, 2H), 7.38-7.41 (m, 2H), 7.20-7.36 (m, 16H), 5.54 (d, $J = 2.0$ Hz, 0.33H anomeric), 5.53 (d, $J = 2.0$ Hz, 0.67H anomeric), 4.88 (d, $J = 11.0$ Hz, 0.33H), 4.87 (d, $J = 10.5$ Hz, 0.67H), 4.77 (d, $J = 11.5$ Hz, 1H), 4.65-4.70 (m, 2H), 4.46-4.56 (m, 3H), 4.28-4.34 (m, 1H), 4.19 (br s, 0.33H), 3.97-4.02 (m, 1H), 3.74-3.88 (m, 3H), 3.53 (td, $J = 10.5, 4.5$ Hz, 0.67H), 2.14 (septd, $J = 7.0, 3.0$ Hz, 0.67H), 1.92-1.97 (m, 0.67H), 1.66-1.77 (m, 0.67H), 1.43-1.63 (m, 1.67H), 1.20-1.35 (m, 1.67H), 1.11 (ddt, $J = 12.25, 9.75, 2.75$ Hz, 0.67H), 0.72-1.04 (m, 4H), 0.83 (d, $J = 7.0$ Hz, 3H_{major}), 0.82 (d, $J = 6.5$ Hz, 3H_{major}), 0.80 (d, $J = 7.0$ Hz, 3H_{minor}), 0.78 (d, $J = 6.5$ Hz, 3H_{minor}), 0.71 (d, $J = 7.0$ Hz, 3H_{major}), 0.17 (s, 3H_{major}), 0.16 (s, 3H_{minor}), 0.15 (s, 3H_{major + minor}), Note – diastereomers are reported as a 2:1 ratio of the total amount of protons, the stereochemistry of the major diastereomer and the dr of the reduction was determined on a crude reaction mixture of the silyl-linked compound after complete desilylation by *n*-Bu₄NF and comparison to known compounds;^{4,5} ^{13}C NMR (100 MHz, CDCl_3) major and minor diastereomer signals reported δ 138.53, 138.47, 138.43, 138.3, 138.2, 134.74, 134.66, 131.7, 131.4, 131.3, 128.9, 128.8, 128.3, 128.2, 127.92, 127.85, 127.77, 127.66, 127.63, 127.58, 127.35, 127.12, 127.09, 89.3, 89.0, 80.3, 75.03, 74.85, 73.16, 73.13, 72.99, 72.86, 72.6, 72.2, 72.1, 70.7, 70.6, 69.28, 69.24, 68.8, 49.8, 48.6, 45.3, 43.1, 35.1, 34.4, 31.6, 28.8, 25.7, 25.5, 25.3, 24.0, 22.8, 22.4, 22.2, 21.1, 21.0, 20.8, 15.8, -1.20, -1.22, -1.36, -1.40; IR (film, cm^{-1}) 3029, 2952, 2915, 2866, 1453, 1255, 1099; HRMS (ES) m/z calcd for $\text{C}_{45}\text{H}_{58}\text{O}_8\text{SSi}$ $[\text{M}+\text{Na}]^+$ 777.3621, found 777.3640.

[4-phenylbutan-2]-3,4,6-tri-*O*-benzyl- α -D-glucopyranoside (Table 1, compound 6a)



Following the general procedure, compound **4a** (112 mg, 0.16 mmol), NIS (47 mg, 0.21 mmol), TMSOTf (35 μ L, 0.19 mmol), 2,6-DTBMP (66 mg, 0.32 mmol) were stirred for 10 min at -40 $^{\circ}$ C, and 30 min at 0 $^{\circ}$ C, then excess *n*-Bu₄NF (0.96 mmol, 0.96 mL) was added as a 1M solution in THF and stirred overnight to afford the desired products as a 46:54 mixture of diastereomers as clear oils, which were separated and characterized independently (combined 90 mg, 0.15 mmol, 97%, 54:46) upon purification by flash chromatography on SiO₂ (20% EtOAc/Hex). **Major diastereomer** ¹H NMR (500 MHz, CDCl₃) δ 7.39-7.42 (m, 2H), 7.25-7.36 (m, 13H), 7.13-7.21 (m, 5H), 5.02 (d, *J* = 3.0 Hz, 1H anomeric), 4.97 (d, *J* = 11.0 Hz, 1H), 4.85 (d, *J* = 10.0 Hz, 1H), 4.83 (d, *J* = 10.5 Hz, 1H), 4.62 (d, *J* = 12.5 Hz, 1H), 4.49 (d, *J* = 10.5 Hz, 1H), 4.47 (d, *J* = 12.0 Hz, 1H), 3.83-3.92 (m, 2H), 3.58-3.76 (m, 5H), 2.70-2.78 (m, 1H), 2.60-2.68 (m, 1H), 1.92-2.07 (m, 2H), 1.77-1.85 (m, 1H), 1.23 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 141.8, 138.8, 138.2, 137.9, 128.35, 128.34, 128.32, 128.27, 127.9, 127.8, 127.66, 127.63, 127.56, 125.8, 96.0, 83.6, 77.3, 75.3, 75.0, 73.5, 72.8, 72.7, 70.8, 68.4, 38.6, 32.0, 19.1; IR (film, cm⁻¹) 3461, 3061, 3029, 2924, 1495, 1453, 1381, 1129, 1065, 1034 ; HRMS (ES) *m/z* calcd for C₃₇H₄₂O₆ [M+Na]⁺ 605.2879, found 605.2877. **Minor diastereomer** ¹H NMR (500 MHz, CDCl₃) δ 7.39-7.42 (m, 2H), 7.26-7.36 (m, 13H), 7.18-7.22 (m, 3H), 7.14-7.17 (m, 2H), 4.99 (d, *J* = 3.5 Hz, 1H anomeric), 4.96 (d, *J* = 11.5 Hz, 1H), 4.84 (d, *J* = 10.5 Hz, 1H), 4.83 (d, *J* = 10.5 Hz, 1H), 4.65 (d, *J* = 12.5 Hz, 1H), 4.50 (d, *J* = 12 Hz, 1H), 4.49 (d, *J* = 10.5 Hz, 1H), 3.89 (d, *J* = 9.0 Hz, 1H), 3.62-3.83 (m, 6H), 2.64-2.75 (m, 2H), 1.90-1.98 (m, 2H), 1.74-1.82 (m, 1H), 1.28 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 141.7, 138.8, 138.1, 137.9, 128.42, 128.35, 128.32, 128.27, 127.93, 127.87, 127.83, 127.70, 127.63, 127.59, 125.9, 98.5, 83.5, 77.4, 75.28, 75.26, 75.0, 73.5, 73.2, 70.6, 68.5, 38.0, 31.5, 21.3; IR (film, cm⁻¹) 3559, 3471, 3029, 2922, 2864, 1454, 1363, 1129, 1066, 1036; HRMS (ES) *m/z* calcd for C₃₇H₄₂O₆ [M+Na]⁺ 605.2879, found 605.2876.

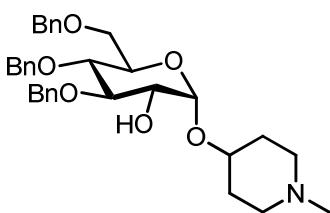
8-(1,4-dioxaspiro[4.5]decane)-3,4,6-tri-*O*-benzyl- α -D-glucopyranoside (Table 1, compound **6b)**



Following the general procedure, compound **4b** (425 mg, 0.60 mmol), NIS (175 mg, 0.78 mmol), 2,6-DTBMP (185 mg, 0.90 mmol), TMSOTf (142 μ L, 0.78 mmol) were stirred for 10 min at -40 $^{\circ}$ C, then warmed to 0 $^{\circ}$ C and allowed to stir for 1 hour. *n*-Bu₄NF (3.0 mL, 3.0 mmol) was added as a 1M solution in THF, warmed to rt and stirred overnight.

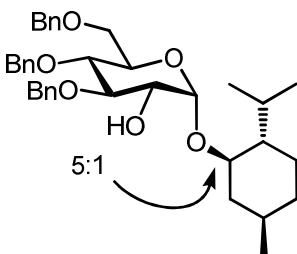
The product (289 mg, 0.49 mmol, 82%) was obtained as a colorless oil after flash chromatography on SiO₂ (33% EtOAc/Hex w/ 5% NEt₃). ¹H NMR (400 MHz, CDCl₃) δ 7.22-7.38 (m, 13 H), 7.10-7.14 (m, 2H), 4.98 (d, *J* = 3.2 Hz, 1H anomeric), 4.94 (d, *J* = 11.2 Hz, 1H), 4.80 (d, *J* = 10.8 Hz, 2H), 4.61 (d, *J* = 12.0 Hz, 1H) 4.47 (d, *J* = 12.0 Hz, 1H) 4.45 (d, *J* = 10.8 Hz, 1H), 3.89-3.93 (m, 4H), 3.84 (ddd, *J* = 10.0, 3.2, 2.0 Hz, 1H), 3.57-3.66 (m, 6H), 1.96 (d, *J* = 10.0 Hz, 1H) 1.66-1.91 (m, 6H), 1.50-1.59 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 138.7, 138.1, 137.9, 128.33, 128.31, 127.9, 127.84, 127.80, 127.7, 127.63, 127.56, 108.0, 97.0, 83.6, 75.3, 75.0, 73.5, 73.4, 72.9, 70.6, 68.4, 64.3, 64.2, 31.6, 31.3, 29.9, 28.1; IR (film, cm⁻¹) 3476, 3029, 2937, 1496, 1453, 1365, 1134, 1068, 1028; HRMS (ES) *m/z* calcd for C₃₅H₄₂O₈ [M+Na]⁺ 613.2777, found 613.2786.

4-(methylpiperidin-1)-3,4,6-tri-*O*-benzyl- α -D-glucopyranoside (Table 1, compound 6c)



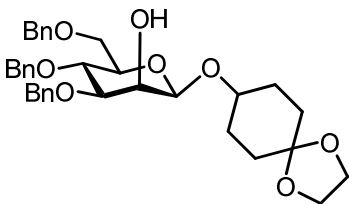
Following the general procedure, compound 4c (125 mg, 0.19 mmol), NIS (55 mg, 0.24 mmol), 2,6-DTBMP (77 mg, 0.38 mmol), TMSOTf (41 μ L, 0.23 mmol) were stirred at -40 °C for 10 min, then warmed to 0 °C and stirred for 1 hour, then excess *n*-Bu₄NF was added (1.14 mL, 1.14 mmol) as a 1M solution in THF, warmed to rt and allowed to stir overnight. The product (73 mg, 0.13 mmol, 70%) was obtained after purification by flash chromatography on SiO₂ (7:1:2 to 3:1:1 EtOAc:MeOH:MeCN w/ ~ 1% NEt₃). ¹H NMR (500 MHz, CDCl₃) δ 7.39-7.42 (m, 2H), 7.26-7.37 (m, 11H), 7.13-7.16 (m, 2H), 5.03 (d, *J* = 3.5 Hz, 1H anomeric), 4.99 (d, *J* = 11.0 Hz, 1H), 4.85 (d, *J* = 11.0 Hz, 1H), 4.84 (d, *J* = 10.5 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.51 (d, *J* = 11.5 Hz, 1H), 4.49 (d, *J* = 10.5 Hz, 1H), 3.87 (ddd, *J* = 10.0, 3.75, 1.75 Hz, 1H), 3.61-3.79 (m, 6H), 2.68 (br s, 2H), 2.28 (s, 3H), 2.20 (br s, OH), 2.16 (br s, 2H), 1.92 (br s, 1H), 1.62-1.77 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 138.7, 138.0, 137.9, 128.40, 128.37, 128.36, 128.0, 127.9, 127.84, 127.77, 127.69, 127.6, 97.1, 83.6, 77.3, 75.3, 75.1, 73.5, 72.9, 70.7, 68.5, 53.1, 46.1, 32.5, 30.8; IR (film, cm⁻¹) 3453, 3030, 2920, 2850, 2784, 1452, 1384, 1155, 1068, 1043; HRMS (ES) *m/z* calcd for C₃₃H₄₁NO₆ [M+H]⁺ 548.3012, found 548.3019.

(1*R*,2*S*,4*S*)-2-isopropyl-4-methylcyclohexan-3,4,6-tri-*O*-benzyl- α -D-glucopyranoside (Table 1, compound 6d)



Following the general procedure, compound **4e** (87 mg, 0.12 mmol), NIS (34 mg, 0.15 mmol), 2,6-DTBMP (47 mg, 0.24 mmol) and TMSOTf (25 μ L, 0.14 mmol) were stirred for 10 min at -40 $^{\circ}$ C, warmed to 0 $^{\circ}$ C and stirred for 45 min, then excess *n*-Bu₄NF was added (0.72 mL, 0.72 mmol) as a 1M solution in THF, warmed to rt, and stirred overnight. The product (49 mg, 0.08 mmol, 72%, 5:1) was obtained as an inseparable 5:1 mixture of diastereomers as a colorless oil after purification by flash chromatography on SiO₂ (10 to 20% EtOAc/Hex). ¹H NMR (500 MHz, CDCl₃) **Major diastereomer** δ 7.26-7.43 (m, 13H), 7.14-7.18 (m, 2H), 4.99 (d, *J* = 4.0 Hz, 1H anomeric), 4.98 (d, *J* = 12.0 Hz, 1H), 4.85 (d, *J* = 11.5 Hz, 1H), 4.84 (d, *J* = 10.5 Hz, 1H), 4.66 (d, *J* = 12.0 Hz, 1H), 4.51 (d, *J* = 11.0 Hz, 1H), 4.48 (d, *J* = 10.5 Hz, 1H), 3.95 (d, *J* = 10.0 Hz, 1H), 3.60-3.84 (m, 5H), 3.41 (td, *J* = 10.5, 4.0 Hz, 1H), 2.21 (d, *J* = 12.5 Hz, 1H), 2.15 (septd, *J* = 7.0, 2.0 Hz, 1H), 1.97 (d, *J* = 9.0 Hz, 1H), 1.56-1.80 (m, 2H), 1.24-1.46 (m, 2H), 0.78-1.05 (m, 3H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.87 (d, *J* = 7.0 Hz, 3H), 0.78 (d, *J* = 7.0 Hz, 3H), diagnostic peaks of the minor diastereomer at 5.03 (d, *J* = 3.5 Hz, 0.2H anomeric), and 4.11 (br s, 0.2H) (aglycone carbinol); ¹³C NMR (100 MHz, CDCl₃) major and minor diastereomer signals reported δ 138.8, 138.2, 138.0, 128.36, 128.33, 128.11, 127.96, 127.92, 127.85, 127.7, 127.64, 127.60, 100.1, 95.4, 83.5, 81.1, 77.5, 75.2, 75.0, 73.6, 73.5, 73.0, 72.6, 70.6, 68.6, 48.7, 48.2, 42.9, 37.3, 34.9, 34.2, 31.6, 28.4, 26.4, 25.5, 22.8, 22.2, 21.2, 21.1, 20.9, 15.7; IR (film, cm⁻¹) 3564, 3030, 2922, 2867, 1453, 1384, 1132, 1067, 1027; HRMS (ES) *m/z* calcd for C₃₇H₄₈O₆ [M+Na]⁺ 611.3349, found 611.3355.

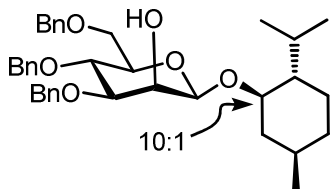
8-(1,4-dioxaspiro[4.5]decane)-3,4,6-tri-*O*-benzyl- β -D-mannopyranoside (Table 1, compound 7a)



Following the general procedure, compound **5a** (144 mg, 0.20 mmol) NIS (59 mg, 0.26 mmol), 2,6-DTBMP (83 mg, 0.41 mmol) and TMSOTf (44 μ L, 0.24 mmol) were stirred at -40 $^{\circ}$ C for 15 minutes, warmed to 0 $^{\circ}$ C and stirred for 45 min, then *n*-Bu₄NF (1.2 mL, 1.2 mmol) was added as a 1M solution in THF and the reaction was warmed to rt and stirred overnight. The product (67 mg, 0.11 mmol, 57%) was obtained as a colorless oil upon purification by flash chromatography on SiO₂ (40 to 50% EtOAc/Hex). ¹H NMR (500 MHz, CDCl₃) δ 7.38-7.41 (m, 2H), 7.26-7.36 (m, 11H), 7.21-7.24 (m, 2H), 4.91 (d, *J* = 11.0 Hz, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 11.0 Hz, 1H), 4.52 (s, 1H anomeric), 4.07 (br s, 1H), 3.89-3.98 (m, 5H), 3.86 (t, *J* = 9.5 Hz, 1H), 3.78 (dd, *J* = 10.5, 1.5 Hz, 1H), 3.69 (dd, *J* = 10.5, 5.5 Hz, 1H), 3.58 (dd, *J* = 9.0, 3.0 Hz, 1H), 3.43 (ddd, *J* = 9.5, 5.5, 1.5 Hz, 1H), 2.45 (d, *J* = 1.5 Hz, 1H), 1.70-1.98 (m, 6H), 1.52-1.61 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 138.3, 138.2, 137.9, 128.5, 128.35, 128.31, 128.1, 127.9, 127.8, 127.7, 127.5, 108.2, 97.4, 81.6, 75.23, 75.16, 74.3, 73.7, 73.4, 71.3, 69.3, 68.8, 64.3, 31.4, 31.3, 29.9, 27.9; IR (film, cm⁻¹)

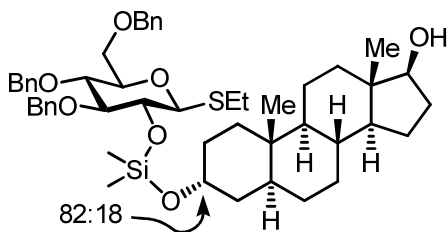
¹) 3476, 3029, 2940, 2872, 1452, 1372, 1100; HRMS (ES) *m/z* calcd for C₃₅H₄₂O₈ [M+Na]⁺ 613.2777, found 613.2781.

(1R,2S,4S)-2-isopropyl-4-methylcyclohexan-3,4,6-tri-*O*-benzyl-β-D-mannopyranoside (Table 1, compound 7b)



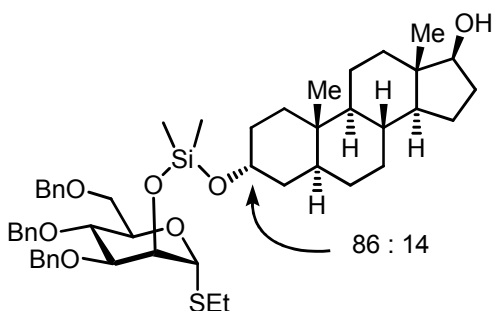
Following the general procedure, compound **5b** (68 mg, 0.09 mmol), NIS (26 mg, 0.12 mmol), 2,6-DTBMP (37 mg, 0.18 mmol), and TMSOTf (20 μL, 0.11 mmol) were stirred at -40 °C for 10 min, then warmed to 0 °C and stirred for 1.5 hours. *n*-Bu₄NF (0.63 mL, 0.63 mmol) was added as a 1M solution in THF and stirred at rt overnight to give the products as a 10:1 mixture of diastereomers. The products (combined 39 mg, 0.07 mmol, 74%, 10:1) were isolated as a white solid and clear oil respectively, and characterized independently after purification by flash chromatography on SiO₂ (10 to 20% EtOAc/Hex). Data for the major diastereomer matches that previously reported.⁶ **Major diastereomer** ¹H NMR (500 MHz, CDCl₃) δ 7.38-7.41 (m, 2H), 7.24-7.36 (m, 13H), 4.91 (d, *J* = 11.0 Hz, 1H), 4.80 (d, *J* = 12.0 Hz, 1H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 12.5 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.54 (s, 1H anomeric), 4.04 (br s, 1H), 3.87 (t, *J* = 9.5 Hz, 1H), 3.75 (dd, *J* = 10.5, 1.5 Hz, 1H), 3.71 (dd, *J* = 10.5, 5.0 Hz, 1H), 3.55-3.63 (m, 2H), 3.41 (ddd, *J* = 10.0, 5.0, 2.0 Hz, 1H), 2.38 (s, 1H), 2.29 (septd, *J* = 7.0, 2.0 Hz, 1H), 1.99 (d, *J* = 12.0 Hz, 1H), 1.62-1.70 (m, 2H), 1.24-1.41 (m, 2H), 0.80-1.05 (m, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.91 (d, *J* = 7.0 Hz, 3H), 0.83 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 138.4, 138.3, 138.0, 128.44, 128.35, 128.29, 128.16, 127.8, 127.75, 127.71, 127.68, 127.5, 96.1, 81.9, 76.5, 75.3, 75.2, 74.4, 73.6, 71.2, 69.7, 69.2, 47.7, 40.4, 34.3, 31.3, 25.3, 23.1, 22.3, 21.0, 15.8; IR (film, cm⁻¹) 3472, 3028, 2950, 2920, 2865, 1452, 1383, 1102; HRMS (ES) *m/z* calcd for C₃₇H₄₈O₆ [M+Na]⁺ 611.3349, found 611.3337. **Minor diastereomer** ¹H NMR (500 MHz, CDCl₃) δ 7.38-7.42 (m, 2H), 7.23-7.36 (m, 13H), 4.91 (d, *J* = 11 Hz, 1H), 4.81 (d, *J* = 12 Hz, 1H), 4.69 (d, *J* = 11.5 Hz, 1H), 4.64 (d, *J* = 12 Hz, 1H), 4.58 (d, *J* = 11 Hz, 1H), 4.57 (d, *J* = 12 Hz, 1H), 4.44 (s, 1H anomeric), 4.07 (d, *J* = 2.5 Hz, 1H), 4.02 (br s, 1H), 3.69 (t, *J* = 9.0 Hz, 1H), 3.74 (dd, *J* = 11, 2.0 Hz, 1H), 3.70 (dd, *J* = 11, 5.5 Hz, 1H), 3.56 (dd, *J* = 9.5, 3.0 Hz, 1H), 3.41 (ddd, *J* = 9.5, 5.0, 2.0 Hz, 1H), 2.39 (br s, 1H), 2.16-2.22 (m, 1H), 1.81-1.91 (m, 1H), 1.69-1.86 (m, 1H), 1.60-1.68 (m, 1H), 1.20-1.44 (m, 2H), 0.80-1.00 (m, 3H), 0.90 (d, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 7.0 Hz, 3H), 0.85 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 138.4, 138.3, 138.0, 128.42, 128.35, 128.31, 128.1, 127.9, 127.73, 127.69, 127.65, 127.5, 101.3, 81.8, 78.5, 75.3, 75.2, 74.3, 73.6, 71.3, 69.5, 69.0, 48.3, 41.1, 35.0, 28.9, 26.2, 24.6, 22.4, 21.3, 20.9; IR (film, cm⁻¹) 3444, 3027, 2917, 2848, 1452, 1383, 1103; HRMS (ES) *m/z* calcd for C₃₇H₄₈O₆ [M+Na]⁺ 611.3349, found 611.3359.

Ethyl 2-*O*-[(3*R*,5*S*,8*R*,9*S*,10*S*,13*S*,14*S*,17*S*)-3-(dimethylsilyloxy)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-ol]-3,4,6-tri-*O*-benzyl-1-thio- β -D-glucopyranoside (Scheme 3, compound 8a)



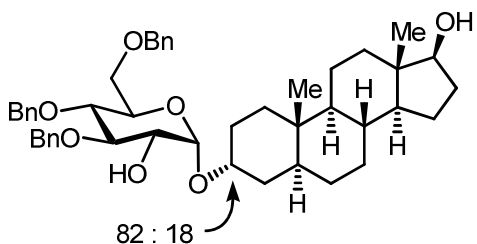
Following the general procedure, **1a** (182 mg, 0.33 mmol), dihydrotestosterone⁷ (87 mg, 0.30 mmol), Ni(COD)₂ (8 mg, 0.03 mmol), IMes·HCl (10 mg, 0.03 mmol), KO-*t*-Bu (3.4 mg, 0.03 mmol), and Ti(O-*i*-Pr)₄ (195 μ L, 0.66 mmol) were stirred for 6.5 hr at rt to give the product as an inseparable 5:1 mixture of diastereomers. The product (226 mg, 0.27 mmol, 89%, 5:1) was obtained as a viscous yellow oil after flash chromatography on SiO₂ (20 to 25% EtOAc/Hex). ¹H NMR 7.24-7.40 (m, 13H), 7.06 (m, 2H), 5.03 (d, *J* = 11.5 Hz, 1H), 4.86 (d, *J* = 11.5 Hz, 1H), 4.71 (d, *J* = 11.0 Hz, 1H), 4.61 (d, *J* = 12.5 Hz, 1H), 4.56 (d, *J* = 12.5 Hz, 1H), 4.51 (d, *J* = 10.5 Hz, 1H), 4.40 (d, *J* = 9.5 Hz, 1H anomeric), 4.17 (t, *J* = 2.5 Hz, 1H) 3.47-3.81 (m, 7H_{major + minor}), 2.68-2.81 (m, 2H), 2.00-2.10 (m, 1H), 0.56-1.82 (m, 31H_{major + minor}) {assignable peaks within this multiplet: 1.32 (t, *J* = 7.5 Hz, 3H_{major}), 0.73 (s, 3H_{major}), 0.71 (s, 3H_{major})}, 0.21 (s, 3H), 0.19 (s, 3H), diagnostic peaks for minor diastereomer 4.97 (d, *J* = 11.5 Hz, 1H_{minor}), 4.90 (d, *J* = 11 Hz, 1H_{minor}) benzylic, Note – the stereochemistry of the major diastereomer and the dr of the reduction was determined on a crude reaction mixture of the silyl-linked compound after complete desilylation by *n*-Bu₄NF and comparison to known compounds;^{8,9} ¹³C NMR (100 MHz, CDCl₃) major and minor diastereomer signals reported δ 138.9, 138.2, 138.0, 128.34, 128.31, 128.2, 127.95, 127.93, 127.72, 127.69, 127.5, 127.3, 127.0, 87.2, 87.0, 86.2, 82.0, 79.1, 78.3, 78.1, 75.3, 75.1, 74.9, 74.6, 73.4, 71.7, 69.1, 67.2, 54.5, 54.1, 51.01, 50.95, 44.9, 42.9, 38.8, 38.2, 37.1, 36.74, 36.67, 36.4, 35.9, 35.5, 35.4, 32.3, 31.64, 31.57, 31.47, 30.5, 29.7, 29.4, 28.6, 28.4, 24.7, 23.4, 23.3, 20.7, 20.3, 15.1, 12.3, 11.4, 11.1, -0.9, -1.0, -1.1, -1.2; IR (film, cm⁻¹) 3429, 3028, 2925, 2867, 1496, 1452, 1362, 1253, 1133, 1067, 1027; HRMS (ES) *m/z* calcd for C₅₀H₇₀O₇SSi [M+Na]⁺ 865.4509, found 865.4501.

Ethyl 2-*O*-[(3*R*,5*S*,8*R*,9*S*,10*S*,13*S*,14*S*,17*S*)-3-(dimethylsilyloxy)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-ol]-3,4,6-tri-*O*-benzyl-1-thio- α -D-mannopyranoside (Scheme 3, compound 8b)



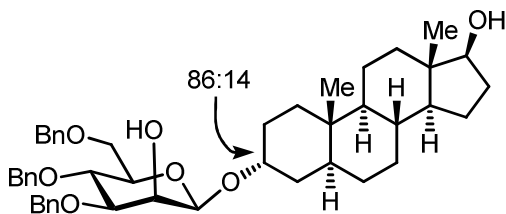
Following the general procedure, **2a** (182 mg, 0.33 mmol) dihydrotestosterone⁷ (87 mg, 0.30 mmol), Ni(COD)₂ (8 mg, 0.03 mmol), IMes·HCl (10 mg, 0.03 mmol), KO-*t*-Bu (3.4 mg, 0.03 mmol), and Ti(*O-i*-Pr)₄ (195 μ L, 0.66 mmol) were stirred for 6.5 hr at rt to give the desired product as an inseparable 6:1 mixture of diastereomers. The product (202 mg, 0.24 mmol, 80%, 6:1) was obtained as a viscous off-white oil after flash chromatography on SiO₂ (10 to 20% EtOAc/hexanes). ¹H NMR (500 MHz, CDCl₃) **Major diastereomer** δ 7.24-7.38 (m, 13H), 7.15-7.18 (m, 2H), 5.32 (d, J = 1.5 Hz, 1H anomeric), 4.84 (d, J = 11.0 Hz, 1H), 4.73 (d, J = 11.5 Hz, 1H), 4.69 (d, J = 12.0 Hz, 1H), 4.62 (d, J = 12.0 Hz, 1H), 4.52 (d, J = 11.0 Hz, 1H), 4.50 (d, J = 10.5 Hz, 1H), 4.30 (dd, J = 2.5, 2.0 Hz, 1H), 4.12-4.16 (m, 2H), 3.98 (t, 9.5 Hz, 1H), 4.83 (dd, J = 11.0, 5.0 Hz, 1H), 3.77 (dd, J = 9.0, 2.25 Hz, 1H), 3.72 (dd, J = 11.0, 2.0 Hz, 1H), 3.62 (t, J = 8.25 Hz, 1H), 2.54-2.70 (m, 2H), 2.01-2.11 (m, 1H), 1.78 (dt, J = 12.5, 3.5 Hz, 1H), 1.09-1.66 (m, 17H), 1.29 (t, J = 7.5 Hz, 3H), 1.02, (td, J = 13.0, 4.0 Hz, 1H), 0.80-0.96 (m, 2H), 0.69-0.78 (m, 1H), 0.76 (s, 3H), 0.73 (s, 3H), 0.16 (s, 3H), 0.15 (s, 3H); diagnostic peak for minor diastereomer at 5.28 (d, J = 1.5 Hz, 0.15H anomeric), Note – the stereochemistry of the major diastereomer and the dr of the reduction was determined on a crude reaction mixture of the silyl-linked compound after complete desilylation by *n*-Bu₄NF and comparison to known compounds;^{8,9} ¹³C NMR (100 MHz, CDCl₃) major and minor diastereomer signals reported δ 138.5, 138.3, 128.3, 128.2, 127.9, 127.7, 127.6, 127.5, 127.4, 85.5, 82.0, 80.4, 74.9, 74.8, 73.2, 72.1, 72.0, 70.6, 69.2, 67.0, 54.3, 51.1, 44.9, 43.0, 39.0, 36.7, 36.4, 36.0, 35.5, 25.3, 23.3, 20.3, 15.1, 11.4, 11.1, -1.4, -1.5, -1.7; IR (film, cm⁻¹) 3465, 3030, 2925, 1452, 1371, 1255, 1097, 1047; HRMS (ES) m/z calcd for C₅₀H₇₀O₇SSi [M+Na]⁺ 865.4509, found 865.4484.

3-(3R,5S,8R,9S,10S,13S,14S,17S)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthrene-17-ol 3,4,6-tri-*O*-benzyl- α -D-glucopyranoside (Scheme 3, compound 9a)



Following the general procedure, compound **8a** (145 mg, 0.17 mmol), NIS (54 mg, 0.24 mmol), TMSOTf (75 μ L, 0.41 mmol), 2,6-DTBMP (141 mg, 0.69 mmol) were stirred for 5 minutes at -40 $^{\circ}$ C, and 1 hour at 0 $^{\circ}$ C then excess *n*-Bu₄NF (1.7 mL, 1.7 mmol) was added as a 1M solution in THF and stirred overnight to afford the desired products as a 5:1 mixture of diastereomers. The products (combined 117 mg, 0.16 mmol, 95%, 5:1) were obtained as colorless viscous oils, separated and characterized independently upon purification by flash chromatography on SiO₂ (30 to 40% EtOAc/Hex). **Major diastereomer** ¹H NMR (500 MHz, CDCl₃) δ 7.41-7.44 (m, 2H), 7.26-7.38 (m, 11H), 7.14-7.17 (m, 2H), 5.02 (d, *J* = 11.0 Hz, 1H), 4.97 (d, *J* = 3.5 Hz, 1H anomeric), 4.87 (d, *J* = 11.0 Hz, 1H), 4.84 (d, *J* = 10.5 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.50 (d, *J* = 10.5 Hz, 1H), 3.91 (m, 1H), 3.85 (ddd, *J* = 10.0, 3.5, 1.5 Hz, 1H), 3.78 (dd, *J* = 10.5, 3.5 Hz, 1H), 3.68-3.75 (m, 2H), 3.61-3.68 (m, 3H), 2.02-2.11 (m, 1H), 1.96 (d, *J* = 9.5 Hz, 1H), 1.78-1.81 (m, 2H), 1.52-1.70 (m, 4H), 1.13-1.52 (m, 12 H), 1.07 (td, *J* = 13.0, 4.0 Hz, 1H), 0.85-1.02 (m, 2H), 0.80 (s, 3H), 0.74 (s, 3H), 0.70-0.78 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 138.9, 138.1, 138.0, 128.44, 128.37, 128.2, 127.90, 127.87, 127.83, 127.7, 127.6, 97.3, 83.8, 82.0, 77.4, 75.2, 73.5, 73.3, 73.1, 70.7, 68.6, 54.3, 51.0, 43.0, 40.2, 36.7, 36.0, 35.5, 33.1, 32.5, 31.4, 30.5, 28.4, 27.4, 23.3, 20.4, 11.4, 11.1; IR (film, cm⁻¹) 3453, 3063, 3030, 2928, 1496, 1453, 1358, 1135, 1067; HRMS (ES) *m/z* calcd for C₄₆H₆₀O₇ [M+Na]⁺ 747.4237, found 747.4250. **Minor diastereomer** ¹H NMR (500 MHz, CDCl₃) δ 7.37-7.41 (m, 2H), 7.26-7.36 (m, 11H), 7.14-7.17 (m, 2H), 5.03 (d, *J* = 3.5 Hz, 1H anomeric), 4.98 (d, *J* = 11.0 Hz, 1H), 4.84 (d, *J* = 11.0 Hz, 1H), 4.64 (d, *J* = 12.5 Hz), 4.51 (d, *J* = 12.0 Hz, 1H), 4.49 (d, *J* = 10.5 Hz, 1H), 3.90 (ddd, *J* = 10.0, 4.0, 2.0 Hz, 1H), 3.55-3.78 (m, 7H), 2.05 (d, *J* = 9.5 Hz, 1H), 2.02-2.10 (m, 1H), 1.84-1.90 (m, 1H), 1.80 (dt, *J* = 12, 3.5 Hz, 1H), 1.74 (dt, *J* = 13.5, 3.5 Hz, 1H), 1.54-1.68 (m, 3H), 1.20-1.47 (m, 10H), 1.01-1.12 (m, 2H), 0.80-0.98 (m, 3H), 0.82 (s, 3H), 0.74 (s, 3H), 0.60-0.98 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 138.8, 138.2, 138.0, 128.35, 128.33, 127.9, 127.8, 127.7, 127.6, 127.5, 97.0, 83.8, 81.9, 77.4, 75.3, 75.0, 73.5, 73.0, 70.5, 68.7, 54.4, 51.0, 45.0, 43.0, 36.8, 36.7, 36.0, 35.6, 35.5, 31.6, 30.5, 29.7, 28.5, 27.8, 23.4, 20.8, 12.3, 11.1; IR (film, cm⁻¹) 3439, 3029, 2928, 1452, 1356, 1207, 1131, 1067, 1025; HRMS (ES) *m/z* calcd for C₄₆H₆₀O₇ [M+Na]⁺ 747.4237, found 747.4258.

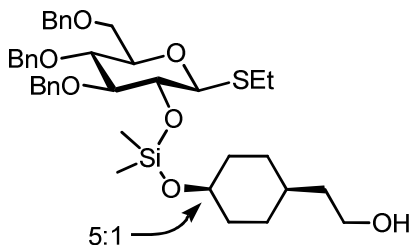
3-(3R,5S,8R,9S,10S,13S,14S,17S)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthrene-17-ol 3,4,6-tri-*O*-benzyl- β -D-mannopyranoside (Scheme 3, compound 9b)



Following the general procedure, compound **8b** (131 mg, 0.16 mmol), NIS (49 mg, 0.22 mmol), 2,6-DTBMP (128 mg, 0.62 mmol), and TMSOTf (68 μ L, 0.37 mmol), were stirred at -40 $^{\circ}$ C for 10 min, then warmed to 0 $^{\circ}$ C and stirred for 1.5 hours. *n*-Bu₄NF (1.6 mL, 1.6 mmol) was then added as a 1M solution in THF, and the reaction was taken to rt

and stirred overnight to give the products as a 6:1 mixture of diastereomers. The products (combined 103 mg, 0.14 mmol, 92%, 6:1) were isolated as viscous, colorless oils, which were separated and characterized independently upon purification by flash chromatography on SiO₂ (30% EtOAc/Hex). **Major diastereomer** ¹H NMR (500 MHz, CDCl₃) δ 7.38-7.41 (m, 2H), 7.24-7.36 (m, 13H), 7.20-7.23 (m, 2H), 4.91 (d, *J* = 11.0 Hz, 1H), 4.81 (d, *J* = 12.0 Hz, 1H), 4.68 (d, *J* = 11.5 Hz, 1H), 4.61 (d, *J* = 12.5 Hz, 1H), 4.56 (d, *J* = 12.5 Hz, 1H), 4.55 (d, *J* = 10.5 Hz, 1H), 4.49 (s, 1H anomeric), 4.09 (br s, 1H), 4.04-4.07 (m, 1H), 3.87 (t, *J* = 9.0 Hz, 1H), 3.76 (dd, *J* = 10.5, 2.0 Hz, 1H), 3.68 (dd, *J* = 11.0, 5.5 Hz, 1H), 3.64 (t, *J* = 8.5 Hz, 1H), 3.59 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.41 (ddd, *J* = 9.5, 5.0, 2.0 Hz, 1H), 2.52 (s, 1H), 2.02-2.11 (m, 1H), 1.79 (dt, *J* = 12.0, 3.0 Hz, 1H), 1.72 (d, *J* = 14.5 Hz, 1H), 1.10-1.68 (m, 18H), 1.05 (td, *J* = 13.0, 4.0 Hz, 1H), 0.85-1.00 (m, 1H), 0.72-0.82 (m, 1H), 0.80 (s, 3H), 0.74 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 138.3, 138.2, 137.9, 128.4, 128.33, 128.28, 128.1, 127.8, 127.74, 127.69, 127.5, 97.2, 81.9, 81.8, 75.2, 75.1, 74.3, 73.5, 72.8, 71.2, 69.3, 68.9, 54.2, 51.0, 42.9, 39.4, 36.7, 35.9, 35.5, 34.2, 32.5, 31.4, 30.5, 28.2, 25.0, 23.3, 20.3, 11.4, 11.1; IR (film, cm⁻¹) 3452, 3028, 2926, 2866, 1452, 1363, 1105, 1056; HRMS (ES) *m/z* calcd for C₄₆H₆₀O₇ [M+Na]⁺ 747.4237, found 747.4250. **Minor diastereomer** ¹H NMR (500 MHz, CDCl₃) δ 7.37-7.40 (m, 2H), 7.27-7.36 (m, 11H), 7.21-7.24 (m, 2H), 4.90 (d, *J* = 11.0 Hz, 1H), 4.78 (d, *J* = 12.0 Hz, 1H), 4.68 (d, *J* = 11.5 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 4.56 (s, 1H anomeric), 4.55 (d, *J* = 11.5 Hz, 1H), 4.06 (s, 1H), 3.83 (t, *J* = 9.75 Hz, 1H), 3.79 (dd, *J* = 10.75, 1.75 Hz, 1H), 3.60-3.75 (m, 2H), 3.68 (dd, *J* = 10.5, 6.0 Hz, 1H), 3.57 (dd, *J* = 9.0, 3.0 Hz, 1H), 3.43 (ddd, *J* = 9.5, 5.75, 1.75 Hz, 1H), 2.46 (d, *J* = 2.0 Hz, 1H), 2.01-2.10 (m, 1H), 1.92-1.98 (m, 1H), 1.80 (dt, *J* = 12.0, 3.25 Hz, 1H), 1.73 (dt, *J* = 13.25, 2.5 Hz, 1H), 1.67 (dq, *J* = 12.75, 3.25 Hz, 1H), 1.20-1.62 (m, 11H), 0.75-1.10 (m, 6H), 0.82 (s, 3H), 0.74 (s, 3H), 0.58-0.65 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 138.4, 138.2, 137.9, 128.5, 128.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.5, 97.2, 82.0, 81.7, 77.4, 75.3, 75.2, 74.4, 73.4, 71.3, 69.4, 68.8, 54.5, 51.0, 44.7, 43.0, 37.0, 36.7, 35.7, 35.5, 34.2, 31.6, 30.5, 29.2, 28.7, 23.4, 20.8, 12.3, 11.1; IR (film, cm⁻¹) 3462, 3028, 2926, 2848, 1452, 1383, 1101, 1071, 1026; HRMS (ES) *m/z* calcd for C₄₆H₆₀O₇ [M+Na]⁺ 747.4237, found 747.4247.

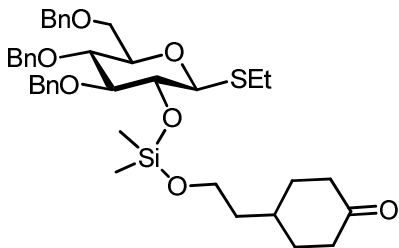
Ethyl 2-*O*-2-(4-(dimethylsilyloxy)cyclohexyl)ethanol -3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (Compound 11, Scheme 4)



Following the general procedure, **1a** (182 mg, 0.33 mmol), hydroxyketone **10**¹⁰ (43 mg, 0.30 mmol), Ni(COD)₂ (8 mg, 0.03 mmol), IMe₃·HCl (10 mg, 0.03 mmol), KO-*t*-Bu (3.4 mg, 0.03 mmol), and Ti(O-*i*-Pr)₄ (195 μL, 0.66 mmol) were stirred for 3 hr at rt to give the desired product **11** as an inseparable 5:1 mixture of diastereomers. Compound **11** (187 mg, 0.26 mmol, 86%, 5:1) was obtained as a viscous colorless oil after purification

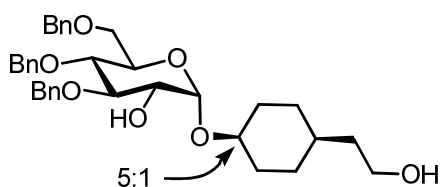
by flash chromatography on SiO₂ (25 to 30% EtOAc/hexanes). ¹H NMR (500 MHz, CDCl₃) δ 7.23-7.39 (m, 13H), 7.07-7.12 (m, 2H), 4.98 (d, *J* = 11.5 Hz, 1H), 4.88 (d, *J* = 11.5 Hz, 1H), 4.73 (d, *J* = 10.5 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 12.5 Hz, 1H), 4.52 (d, *J* = 10.5 Hz, 1H), 4.40 (d, *J* = 9.5 Hz, 1H anomeric), 4.10-4.12 (m, 1H), 3.53-3.78 (m, 7H), 3.49 (ddd, *J* = 9.0, 5.0, 1.75 Hz, 1H), 2.77 (dq, *J* = 12.5, 7.5 Hz, 1H), 2.72 (dq, *J* = 12.5, 7.5 Hz, 1H), 1.59-1.74 (m, 2H), 1.37-1.49 (m, 8H), 1.25-1.39 (m, 1H), 1.32 (t, *J* = 7.5 Hz, 3H), 1.15 (br s, 1H), 0.20 (s, 3H), 0.18 (s, 3H); diagnostic peaks for minor diastereomer: 4.74 (d, *J* = 10.5 Hz, 1H), 1.85-1.97 (m, 1H), 0.22 (s, 3H), 0.17 (s, 3H) Note – the relative stereochemistry of the major and minor diastereomers was confirmed based on the Karplus correlations of the carbinol methine proton of the desilylated diol; ¹³C NMR (100 MHz, CDCl₃) major and minor diastereomer signals reported δ 138.9, 138.2, 138.0, 129.1, 128.34, 128.32, 128.2, 127.9, 127.74, 127.70, 127.6, 127.2, 127.1, 87.1, 87.0, 86.3, 86.1, 79.1, 78.5, 78.2, 75.1, 74.9, 74.5, 73.4, 71.5, 69.2, 67.6, 60.9, 61.1, 39.6, 38.9, 35.5, 33.2, 32.7, 31.4, 27.13, 27.09, 24.7, 15.1, -0.89, -0.90, -1.16, -1.17; IR (film, cm⁻¹) 3437, 3031, 2926, 2858, 1454, 1364, 1255, 1057, 1028; HRMS (ES) *m/z* calcd for C₃₉H₅₄O₇SSi [M+Na]⁺ 717.3257, found 717.3283.

Ethyl 2-*O*- 4-(2-(dimethylsilyloxy)ethyl)cyclohexanone -3,4,6-tri-*O*-benzyl-1-thio-β-*D*-glucopyranoside (Compound 12, Scheme 4)



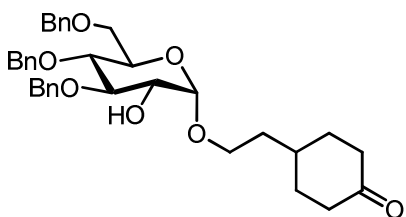
Following the general procedure, **1a** (182 mg, 0.33 mmol), hydroxyketone **10**¹⁰ (43 mg, 0.30 mmol), CuCl (1.5 mg, 0.015 mmol), IMes·HCl (5 mg, 0.015 mmol), and NaO-*t*-Bu (3 mg, 0.03 mmol) were stirred for 3 hr at rt to give the desired product. Compound **12** (119 mg, 0.17 mmol, 57%) was obtained as a colorless oil after purification by flash chromatography on SiO₂ (20% EtOAc/hexanes). ¹H NMR (500 MHz, CDCl₃) δ 7.23-7.38 (m, 13H), 7.08-7.11 (m, 2H), 4.94 (d, *J* = 11.5 Hz, 1H), 4.89 (d, *J* = 11.5 Hz, 1H), 4.73 (d, *J* = 11.0 Hz, 1H), 4.61 (d, *J* = 12.5 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 10.5 Hz, 1H), 4.40 (d, *J* = 9.5 Hz, 1H anomeric), 3.74-3.78 (m, 3H), 3.67-3.72 (m, 2H), 3.62 (t, *J* = 9.25 Hz, 1H), 3.55 (t, *J* = 8.75 Hz, 1H), 3.49 (ddd, *J* = 9.75, 4.75, 1.75 Hz, 1H), 2.77 (dq, *J* = 12.5, 7.5 Hz, 1H), 2.72 (dq, *J* = 12.5, 7.5 Hz, 1H), 2.20-2.38 (m, 4H), 1.93-2.01 (m, 2H), 1.77-1.86 (m, 1H), 1.49 (q, *J* = 7.0 Hz, 2H), 1.28-1.39 (m, 2H), 1.32 (t, *J* = 7.5 Hz, 3H), 0.22 (s, 3H), 0.20 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 212.3, 138.7, 138.2, 137.9, 128.4, 128.34, 128.26, 127.9, 127.78, 127.76, 127.6, 127.3, 127.1, 87.1, 86.2, 79.2, 78.2, 75.2, 75.0, 74.6, 73.5, 69.1, 60.5, 40.8, 38.0, 32.7, 32.6, 32.4, 24.7, 15.1, -1.95, -2.02; IR (film, cm⁻¹) 3031, 2925, 2865, 1715, 1453, 1384, 1256, 1089, 1029; HRMS (ES) *m/z* calcd for C₃₉H₅₂O₇SSi [M+Na]⁺ 715.3101, found 715.3095.

2-(4-cyclohexyl)ethanol-3,4,6-tri-*O*-benzyl-α-*D*-glucopyranoside (Compound 13, Scheme 4)



Following the general procedure, silyl-linked compound **11** (81 mg, 0.12 mmol), NIS (37 mg, 0.16 mmol), 2,6-DTBMP (96 mg, 0.47 mmol), and TMSOTf (51 μ L, 0.28 mmol) were stirred at -40 $^{\circ}$ C for 10 min, then warmed to 0 $^{\circ}$ C and stirred for 1.5 hr. *n*-Bu₄NF (1.2 mL, 1.2 mmol) was added as a 1M solution in THF, warmed to room temperature and stirred over night. The products **13** (combined 67 mg, 0.11 mmol, 97%, 5:1) were isolated as a clear oil and white crystalline solid respectively, and independently characterized after purification by flash chromatography on SiO₂ (50 to 65% EtOAc/hexanes). **Major diastereomer** ¹H NMR (500 MHz, CDCl₃) δ 7.41-7.44 (m, 2H), 7.26-7.37 (m, 11H), 7.14-7.18 (m, 2H), 5.00 (d, *J* = 11.0 Hz, 1H), 4.99 (d, *J* = 4.0 Hz, 1H anomeric), 4.86 (d, *J* = 11.0 Hz, 1H), 4.85 (d, *J* = 10.5 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 12.5 Hz, 1H), 4.51 (d, *J* = 11.0 Hz, 1H), 3.85-3.91 (m, 2H), 3.63-3.80 (m, 7H), 2.00 (d, *J* = 10.0 Hz, 1H), 1.81-1.89 (m, 2H), 1.44 -1.60 (m, 7H), 1.22-1.37 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 138.8, 138.1, 137.9, 128.39, 128.35, 128.34, 128.0, 127.9, 127.85, 127.76, 127.66, 127.58, 97.0, 83.7, 77.3, 75.25, 75.15, 73.5, 73.03, 72.97, 70.6, 68.5, 60.7, 39.0, 32.7, 30.8, 28.7, 27.6, 27.5; IR (film, cm⁻¹) 3436, 3031, 2926, 2860, 1453, 1363, 1132, 1067, 1028; HRMS (ES) *m/z* calcd for C₃₅H₄₄O₇ [M+Na]⁺ 599.2985, found 599.2974. **Minor diastereomer** ¹H NMR (500 MHz, CDCl₃) δ 7.38-7.41 (m, 2H), 7.25-7.36 (m, 11H), 7.13-7.17 (m, 2H), 5.04 (d, *J* = 4.0 Hz 1H anomeric), 4.98 (d, *J* = 11.0 Hz, 1H), 4.84 (d, *J* = 11.5 Hz, 1H), 4.83 (d, *J* = 11.0 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.51 (d, *J* = 11.5 Hz, 1H), 4.49 (d, *J* = 10.5 Hz, 1H), 3.88 (ddd, *J* = 10.0, 3.75, 1.75 Hz, 1H), 3.60-3.79 (m, 7H), 3.56 (tt, *J* = 11.0, 4.25 Hz, 1H), 1.99-2.08 (m, 3H), 1.76-1.85 (m, 2H), 1.48 (q, *J* = 6.5 Hz, 2H), 1.14-1.44 (m, 4H), 0.92-1.04 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 138.8, 138.2, 138.0, 128.38, 128.37, 128.35, 128.0, 127.8, 127.72, 127.66, 127.57, 97.0, 83.7, 77.4, 75.3, 75.1, 73.5, 73.0, 70.5, 68.6, 60.9, 39.4, 33.33, 33.29, 31.7, 31.3, 31.1; IR (film, cm⁻¹) 3401, 3032, 2924, 2853, 1452, 1353, 1130, 1070, 1040; HRMS (ES) *m/z* calcd for C₃₅H₄₄O₇ [M+Na]⁺ 599.2985, found 599.2971.

4-(2-ethyl)cyclohexanone-3,4,6-tri-*O*-benzyl- α -D-glucopyranoside (Compound **14**, Scheme 4)



Following the general procedure, silyl-linked compound **12** (80 mg, 0.12 mmol), NIS (36 mg, 0.16 mmol), 2,6-DTBMP (95 mg, 0.46 mmol), and TMSOTf (50 μ L, 0.28 mmol)

were stirred at -40 °C for 10 min, then warmed to 0 °C and stirred for 30 min. *n*-Bu₄NF (1.2 mL, 1.2 mmol) was added as a 1M solution in THF, warmed to rt and stirred over night. Compound **14** (41 mg, 0.07 mmol, 62%) was obtained as white crystalline solid after purification by flash chromatography on SiO₂ (50 to 60% EtOAc/hexanes). ¹H NMR (500 MHz, CDCl₃) δ 7.38-7.41 (m, 2H), 7.22-7.37 (m, 11H), 7.15-7.19 (m, 2H), 4.95 (d, *J* = 11.0 Hz, 1H), 4.91 (d, *J* = 3.0 Hz, 1H anomeric), 4.88 (d, *J* = 11.0 Hz, 1H), 4.84 (d, *J* = 10.5 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.54 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 10.5 Hz, 1H), 3.71-3.85 (m, 5H), 3.68 (dd, *J* = 10.25, 2.25 Hz, 1H), 3.62 (dd, *J* = 9.5, 9.0 Hz, 1H), 3.56 (dt, *J* = 10.0, 6.5 Hz, 1H), 2.28 (m, 4H), 2.01-2.10 (m, 3H), 1.81-1.91 (m, 1H), 1.60-1.72 (m, 2H), 1.36-1.48 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 211.7, 138.6, 138.0, 137.9, 128.42, 128.37, 128.0, 127.85, 127.82, 127.74, 127.69, 98.5, 83.4, 77.5, 75.3, 75.1, 73.6, 72.9, 70.8, 68.6, 66.2, 40.62, 40.60, 35.1, 32.9, 32.7, 32.4; IR (film, cm⁻¹) 3450, 3031, 2926, 1713, 1453, 1357, 1135, 1068, 1028; HRMS (ES) *m/z* calcd for C₃₅H₄₄O₇ [M+Na]⁺ 597.2828, found 597.2818.

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